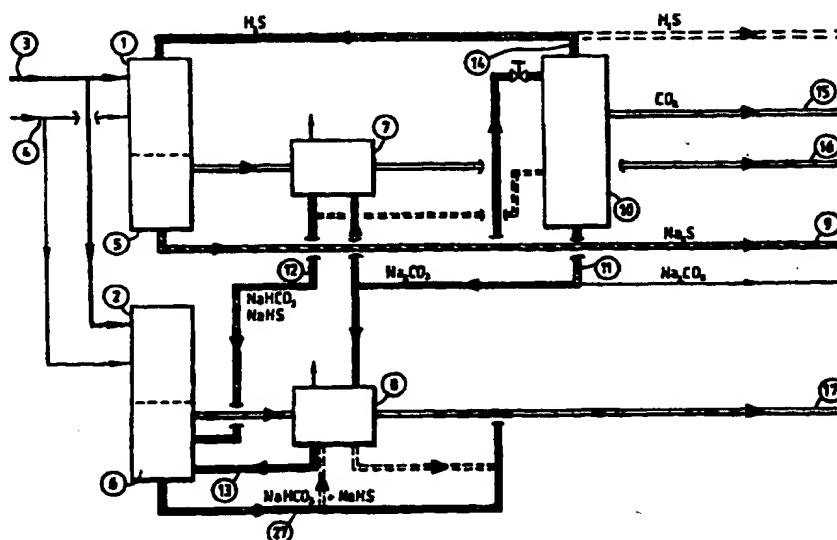




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(21) International Application Number: PCT/SE95/01219 (22) International Filing Date: 18 October 1995 (18.10.95) (30) Priority Data: 9403786-8 4 November 1994 (04.11.94) SE (71) Applicant (for all designated States except US): KVAERNER PULPING TECHNOLOGIES AB [SE/SE]; P.O. Box 1033, S-651 15 Karlstad (SE). (72) Inventor; and (75) Inventor/Applicant (for US only): NILSSON, Bengt [SE/SE]; Gränsvägen 21, S-663 00 Skoghäll (SE). (74) Agent: KYLIN, Peter; Kvaerner Pulping Technologies AB, P.O. Box 1033, S-651 15 Karlstad (SE).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i>

(54) Title: SELECTIVE RECOVERY OF CHEMICALS FROM CELLULOSE SPENT LIQUOR BY LIQUOR GASIFYING

**(57) Abstract**

Process for recovering chemicals and energy from spent liquor obtained when producing paper pulp by chemical delignification of fibrous raw material. The spent liquor is gasified in at least two reactors, a first and a second stream of solid and/or smelt material and of combustible gaseous material being formed. The formed material is treated thereafter in one or more devices (5, 6, 7, 8), whereby a first (9) and a second liquor (27) is formed. The pressure and/or temperature in the said first reactor differ(s) from the pressure and/or temperature in the said second reactor. In addition, one or more process chemicals are recovered selectively from the formed liquor and/or gas, and are thereafter returned in whole or in part to one or more of the said reactors (1, 2) and/or to one or more of the said devices (5, 6, 7, 8) for treatment of the formed material.

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Selective recovery of chemicals from cellulose
spent liquor by liquor gasifying

TECHNICAL FIELD

5 The present invention relates to a process for recovering chemicals and energy from black liquor which is obtained when producing paper pulp by chemical digesting of fibrous raw material.

10 STATE OF THE ART AND PROBLEMS

 When producing paper pulp by the kraft method, a spent liquor is obtained, generally called black liquor, containing organic material and the residual chemicals which have been obtained when digesting the fibrous raw
15 material. This black liquor is generally evaporated and conveyed to a separate processing stage for recovery of the energy content of the organic material and also for recovery of the cooking chemicals as so-called green liquor. The so-called Tomlinson process has for long been
20 the commercially predominant method for this recovery of energy and chemicals. However, a disadvantage of this process, which is by now very old, is that it requires very large combustion furnaces which are complicated from the technical and operational points of view.

25 Swedish Patent SE-C-448 173 describes a more modern process which, in addition to considerably simplifying the necessary process equipment, achieves improved recovery of both energy and chemicals. This process is based on a pyrolysis reaction in which the
30 black liquor is gasified in a so-called Chemrec® reactor, giving an energy-rich gas principally comprising carbon monoxide, carbon dioxide, methane, hydrogen and hydrogen sulphide, as well as inorganic chemicals in the form of small drops of smelt, principally comprising sodium
35 carbonate, sodium hydroxide and sodium sulphide. The resulting mixture of gas and drops of smelt is quickly cooled in a first stage by direct contact with a cooling liquid constituting green liquor, which is formed when

- 2 -

the smelt chemicals and the hydrogen sulphide are dissolved in the cooling liquid. The gas is thereafter washed in a second stage in a gas washer of the scrubber type. The gas is then used as fuel for generating steam
5 and/or electrical power. The physical thermal value of the gas can also be used when the gas is cooled from the gasification temperature to the saturation temperature for steam at the chosen pressure. The green liquor which is formed is conveyed to a causticizing stage for
10 production of white liquor.

SE-B-468 600 discloses a process for producing white liquor of high sulphidity, that is to say with a high proportion of sodium hydrogen sulphide in relation to the proportion of sodium hydroxide, directly from the
15 gasification reactor and without there being any need for causticizing. In accordance with this process, hydrogen sulphide is recovered from the gaseous phase extracted from a reactor of the Chemrec® type and is returned to the reactor in order to be present during the thermal
20 decomposition of the spent liquor. In this way, such a high partial pressure of hydrogen sulphide is established in the gasification stage that the equilibrium reaction



25

is displaced so far to the right that the formation of Na_2CO_3 is suppressed. The Na_2S formed is dissociated to give NaOH and NaHS .

The recovery of hydrogen sulphide from the
30 gaseous phase takes place by means of the gas being allowed to pass through a gas washer containing an external absorption chemical, for example N-methylpyrrolidone or methyldiethylamine, for selective and regenerative absorption of the H_2S content. The need for
35 such an external chemical represents a disadvantage of this process and additionally makes it necessary to

- 3 -

provide a regeneration stag for driving off the hydrogen sulphide from the absorption chemical.

Swedish Patent SE-C-465 039 describes a method which has the object of producing a cooking liquor of
5 high sulphidity. Material containing sulphur and/or material containing sulphur and sodium, which material generally occurs in the pulp mill, is in this case conveyed to a reactor together with the black liquor.

A general disadvantage of previously known
10 recovery techniques is that the recovery of chemicals has been governed by the available process technology. For example, the sulphidity of the white liquor has been adapted to the possibilities of the recovery boiler and not to the requirements of the cooking department. Nor
15 has there been any commercially practicable technique for producing liquor of differing quality for different requirements.

SOLUTION

20 The present invention, which is a refinement of the concept according to SE 448 173 and SE 468 600, provides a process by means of which it is possible, in an extremely flexible manner, to influence the course of the process in the gasification reaction or in subsequent
25 stages of treatment of the reaction products. The said reaction products can in this way be "tailored" for use at different points in the pulp production process. In particular, in a preferred embodiment of the invention, cooking liquor of variable sulphidity can be produced
30 directly. This means in particular that the need for the causticizing and lime sludge reburning, which was necessary in earlier processes, is minimized or completely obviated, since, in accordance with one aspect of the invention, the process involves a form of auto-
35 causticizing.

- 4 -

The principle of the invention is that the black liquor from the pulp digester is conveyed, following evaporation, to a recovery installation where it is divided between two or more gasification reactors, preferably of the Chemrec® type. A high-energy combustion gas is formed in the reactors by means of a known technique, so-called "flash pyrolysis", the said combustion gas principally comprising one or more of the components carbon monoxide, carbon dioxide, methane, hydrogen and hydrogen sulphide, as well as inorganic chemicals in solid form or in the form of small drops of smelt, principally comprising one or more of the components sodium carbonate, sodium hydroxide and sodium sulphide. The resulting mixture of gas and smelt drops is quickly cooled in a treatment device by direct contact with a cooling liquid principally consisting of water and, in certain embodiments, the liquor which is formed when the smelt chemicals and, perhaps some components are dissolved in the cooling liquid. The gas is purified and thereafter washed in one or more gas treatment devices. The liquor which is formed when some of the reaction products are dissolved in the cooling liquid is preferably collected in a treatment device which is connected directly to each reactor and which is of the liquid bath/quench type.

It has now been shown to be possible to recover selectively, from the liquor which is formed, process chemicals which can be used to influence the course of the process in one or more units in the recovery installation. Thus, according to the invention, process chemicals are recovered, preferably by means of one or more absorbers and strippers, from liquor originating from one or more of the gasification reactors. Alternatively, the combustion gas formed in the reactor can be used for recovering process chemicals.

- 5 -

These process chemicals, originating from liquor and/or combustion gas, are then returned, either in whole or in part, to one or more gasification reactors and/or to one or more devices for treatment of combustion gas or solid and/or smelt inorganic material from the reactors. The concept of the invention also includes the fact that at least one reactor operates at a pressure and/or a temperature differing from the pressure and/or temperature in another reactor.

10 A preferred embodiment in this case is that the unit or units to which the recovered process chemicals are returned consist(s) of the gasification reactors, liquid baths/quenchers connected to the latter, or the said devices for purifying and washing the combustion gas. The

15 most preferred embodiment is that the recovered process chemical consists of H_2S and that this is returned to one or more gasification reactors in order to be present during the thermal decomposition of the black liquor, so that the reaction equilibrium (a) is driven towards

20 increased production of Na_2S . Sulphur additionally has a higher affinity towards sodium than it does towards carbon dioxide, for which reason the proportion of Na_2S is further increased and the proportion of Na_2CO_3 decreased. In each reactor, the gasification reaction is

25 controlled, by means of different quantities of returned H_2S , in such a way as to produce a liquor of exactly the quality which is desired. A liquor containing almost 100% Na_2S can be produced, if so desired. This can then be mixed, if appropriate, with causticized Na_2CO_3 , that is to

30 say NaOH, to give the desired quality.

BRIEF DESCRIPTION OF THE FIGURES

Figur 1 shows a block diagram of a preferred embodiment of the invention.

35 Figure 2 shows a possible embodiment of the gas treatment units in Figure 1.

- 6 -

Figure 3 shows a possible embodiment of a liquid bath/quench.

DESCRIPTION OF THE FIGURES

5 Reference number 1 and reference number 2 in Figure 1 each indicate a pressure vessel comprising a ceramically lined gasification reactor. The reactor is provided with an inlet 3 for black liquor and an inlet 4 for oxygen or oxygen-containing gas, as well as a burner
10 (not shown). In both the reactors, the black liquor is decomposed thermally under substoichiometric conditions. The oxygen supply is in this case from almost 0 up to 80%, preferably up to 60%, of the stoichiometrically required quantity of oxygen for complete oxidation of
15 organic and inorganic substance. Each reactor has a liquid bath or quench 5 and 6, respectively, for collecting liquor which is formed when the resulting mixture of gas and smelt from the respective reactor is cooled by direct contact with the cooling liquid
20 principally consisting of water. Each reactor also has a unit 7 and 8, respectively, with gas treatment devices for purifying and washing the combustion gas 16 and 17, respectively. The structure of the gas treatment units is shown in more detail in Figure 2. The combustion gas
25 which leaves the gas treatment units is used as fuel for generating steam and/or electrical power. The physical thermal value of the gas can also be used for generating hot water and/or steam.

Gasification reactor 1 operates at a relatively
30 low pressure (1.5 - 4 bar absolute) with a high partial pressure of H_2S , which means that the reaction equilibrium, in accordance with the same principle as given in SE-B-468 600, is displaced to the right so that the formation of Na_2CO_3 in the solid or smelt phase is
35 suppressed in favour of the formation of Na_2S (see reaction (a) above).

- 7 -

Intensive contact between the combustion gas formed in reactor 1, with its CO₂ content, and the liquor formed when smelt drops and hydrogen sulphide are dissolved in the cooling liquid is avoided as far as possible. It is in this respect preferable for the quench 5 to be designed in accordance with the reactor quench which is described in SE-A0-9402197, that is to say with the outlet from the reactor preferably consisting of a downpipe in which cooling liquid is sprayed directly adjacent to the hot gas outlet through a number of nozzles for maximum contact with the smelt/gas mixture. The cooling liquid consists principally of water or another suitable liquid, which liquid is partially vaporized upon contact with hot gas and smelt at the reactor temperature. The smelt is dissolved in the remaining part of the cooling liquid and in this way forms a liquor which falls down into the liquid bath 5. Alternatively, the smelt falls in the form of drops directly down into the liquid bath 5 and only then is dissolved in the liquor which is already present there. The cooling of the smelt drops then takes place by vaporization of water in the liquid bath.

The downpipe opens out immediately above the liquid level in the liquid bath 5. This is important in order to avoid intensive contact between the gas and the formed liquor. If the pipe had opened out below the surface of the liquid, the gas would have been forced to bubble through the liquor, with the result that undesirable reactions between gas and liquor could have taken place.

By means of this design of reactor and quench, liquor 9 issuing from reactor 1 will contain in the region of 100% Na₂S, dissociated as NaHS and NaOH.

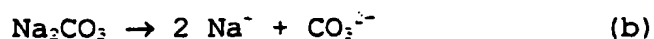
Gasification reactor 2 operates at a comparatively higher pressure (25 bar absolute) and consequently at a higher liquid bath temperature than that of the liquid bath 5 belonging to reactor 1. The



quench/liquid bath 6 belonging to reactor 2 is designed for maximal intensive contact between the combustion gas formed in reactor 2, particularly its content of CO₂ and H₂S, and the green liquor which is formed when smelt drops and hydrogen sulphide are dissolved in the cooling liquid. This is achieved by the downpipe from the reactor being designed for optimal contact between the gas and the cooling liquid in the quench 6. The downpipe is preferably constructed in such a way that it opens out under the surface of the liquid in the quench, as a result of which the gas is forced to bubble intensively through the liquid. A possible embodiment is shown in Figure 3.

Because the temperature in the quench is high and the contact between gas and liquor is forcedly very good, a high proportion of HCO₃⁻ and HS⁻ ions is formed in the green liquor in accordance with reactions (b) - (f) below:

Sodium carbonate in the green liquor is dissociated:



CO₃²⁻ and HCO₃⁻ are included together in the acid/base equilibrium:



This equilibrium is displaced to the right as the temperature is increased, that is to say the solution becomes more alkaline.

At very good contact between carbon dioxide and liquor, the following consecutive reactions subsequently occur:

